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Effect of catalyst pattern geometry on the growth of vertically aligned carbon nanotube arrays**

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Keywords:

CNT chemical-vapor-deposition; nucleation; CVD; vacant arrays

Abstract

We report the effect of catalyst pattern geometry on the growth behavior of carbon nanotube (CNT) vertical arrays. Larger patterns are seen to produce longer CNT arrays. We show that this is predominantly related to the pattern size dependence of the number of walls and relate this to the local availability of carbon feedstock species. In addition, the vertical alignment of CNT-pillar arrays is seen to depend on the pattern design, in particular the relationship between the pillar dimension and the inter-pillar spacing.

1. Introduction

Due to their promising electrical, chemical and mechanical properties, carbon nanotubes (CNT) have been studied for their potential to achieve practical applications in a wide range of areas. During the past decade, there have been considerable efforts towards the development of electron sources ^[1], device stacking components ^[2], composite production ^[3], interconnects for microelectronic chips ^[4] and nano-electro-mechanical-systems ^[5] using vertically standing CNT. Both thermal chemical vapour deposition (TCVD) and plasma enhanced CVD (PECVD) have been used to fabricate arrays of good quality vertically aligned CNT for such purposes, although most studies have focused on the technically simpler TCVD approach. For many applications, it is desirable to produce patterned growth of nanotubes. This is prepared by lithographically patterning the catalyst layer (using photo – or e-beam lithography). However, there have been surprisingly few works about how the pattern geometry may affect the appearance of the CNT arrays, something that has particular importance e.g. for the fabrication of arrays for optimised field emission performance ^[1] or novel composite materials ^[3]. A recent study by Bronikowski ^[6] has shown that the maximum nanotube length achieved in TCVD growth of nanotubes from Fe catalyst with ethylene precursor depends on the catalyst pattern size and spacing. He reported that longer nanotubes could be grown from larger or more densely spaced catalyst patterns. This was interpreted as being due to the influence of an unspecified molecular by-product of ethylene reactions. Hart and Slocum have shown the importance of pre-treatment in iron-catalysed growth from ethylene and the influence of gas flow on the growth of patterned arrays of vertically-aligned MWNT ^[7]. These studies have all focused on ethylene as carbon pre-cursor gas. As discussed convincingly by Eres et al. ^[8], acetylene is an order of magnitude more efficient than other small-molecule precursors and can be regarded as a direct building block for nanotube formation. Acetylene is also the most commonly used precursor for growth of aligned MWNT films. It is therefore of interest to investigate the influence of pattern size on the growth of vertically aligned MWNT from acetylene and to compare the behaviour with that of less efficient precursor gases.

In this paper, we report the results of a systematic study of the effect of catalyst pattern size, spacing and temperature on the growth of vertically aligned carbon nanotube films using acetylene as carbon feedstock. We observe longer carbon nanotube growth from larger catalyst pattern areas, however, the number of walls

also depends on the catalyst pattern area and we show that the total amount of carbon per nanotube is independent of pattern area within the experimental uncertainty. In addition, we observe that the alignment of the nanotube films also depends critically on the catalyst pattern area and the separation between growth areas.

2. Experimental section

Catalyst patterns were defined by electron beam lithography on Si substrates with a thermal oxide layer (400 nm). An aluminum oxide buffer layer (10-nm Al_2O_3) and the catalyst (1-nm Fe) were subsequently deposited by electron beam evaporation. After lift-off, the patterned substrates were inserted into a 40 mm internal diameter quartz tube placed inside a 40cm hot zone furnace to grow CNT films by thermal-CVD. The quartz tube (ca. 60 cm in length) was first evacuated with a mechanical pump and then filled with an argon (900 sccm) and hydrogen (100 sccm) mixture at atmospheric pressure, before being heated to the desired growth temperature. After reaching this temperature, the system was held there for 15 min before introducing the growth gases. A mixture of acetylene, argon, and hydrogen was used to grow the CNT films at atmospheric pressure. The acetylene was initially introduced in a burst corresponding to ca. 90 sccm for a few seconds, settling down to a steady flow of 5 sccm or 3 sccm (specified below) within 10 seconds. The growth temperature was varied in the range of 625 to 750 °C, the temperature window for which vertically aligned carbon nanotubes are produced under our growth conditions. After growth for 15 minutes, the samples were furnace-cooled to room temperature after switching the gases back to argon (900 sccm) and hydrogen (100 sccm). By choosing 15 minutes for the growth window we ensure that in every case, nanotube growth has ceased before the end of the growth window. This was confirmed by checking the length of films grown on different sized catalyst patterns after 15 minutes and 30 minutes growth time. In all cases, the length was the same after 30 minutes growth as after 15 minutes growth. In this way we can quantitatively compare the terminal length of the nanotube films in the present study. For two of the different catalyst patterns growth at 725 °C was also stopped before the end of the growth window, at 5 and 10 min. The height of the nanotubes was determined from scanning electron microscope images (JEOL JSM-6301F) taken with a tilt angle of 60° or 80°.

3. Results and discussions

3.1. Terminal Length Dependence on Pattern Size

Figure 1 shows SEM images illustrating the effect of pattern size on nanotube growth for smaller and larger area of catalyst pattern. The smaller patterns consisted of 50 μm x 50 μm squares where each square was built up from patterns with 1 μm feature-size. The larger patterns were magnified 10 times; hence they consisted of

500 μm x 500 μm squares with the squares built up from patterns with 10 μm feature-size. The same growth conditions (750 $^{\circ}\text{C}$, $\text{C}_2\text{H}_2\text{:Ar:H}_2=5.0\text{:500:500}$ sccm, atmospheric pressure, 15 min growth, and 10 nm Al_2O_3 / 1 nm Fe catalyst film) were used in each case. From a tilt (Fig. 1(a)) and top view (Fig. 1(b)), we see that relatively short CNT arrays reaching ~ 40 μm length with poor alignment were grown from the smaller catalyst patterns. CNT in each growth area are entangled and some reach neighbouring arrays, Fig. 1(c). In contrast, with a ten times larger catalyst pattern, vertically well-aligned, significantly longer CNT arrays are formed (Fig. 1(d) and 1(e)). The length of the CNT arrays in this case reaches ~ 100 μm . Figure 1(f) shows a magnified image of the bottom of the well aligned array.

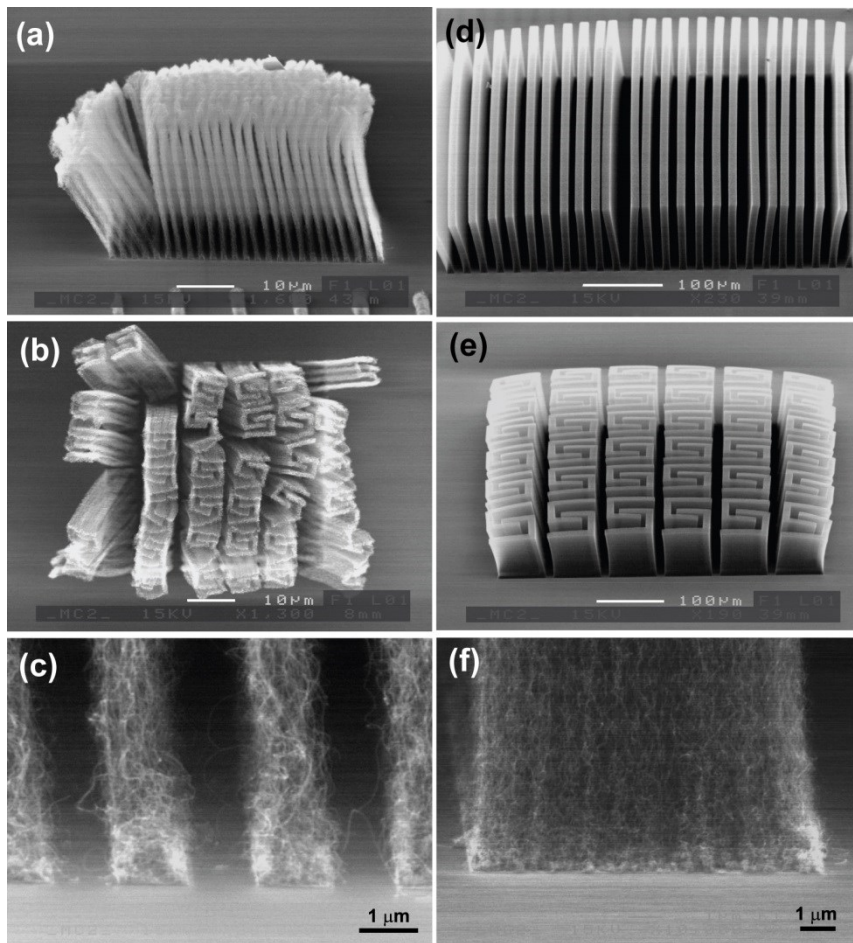
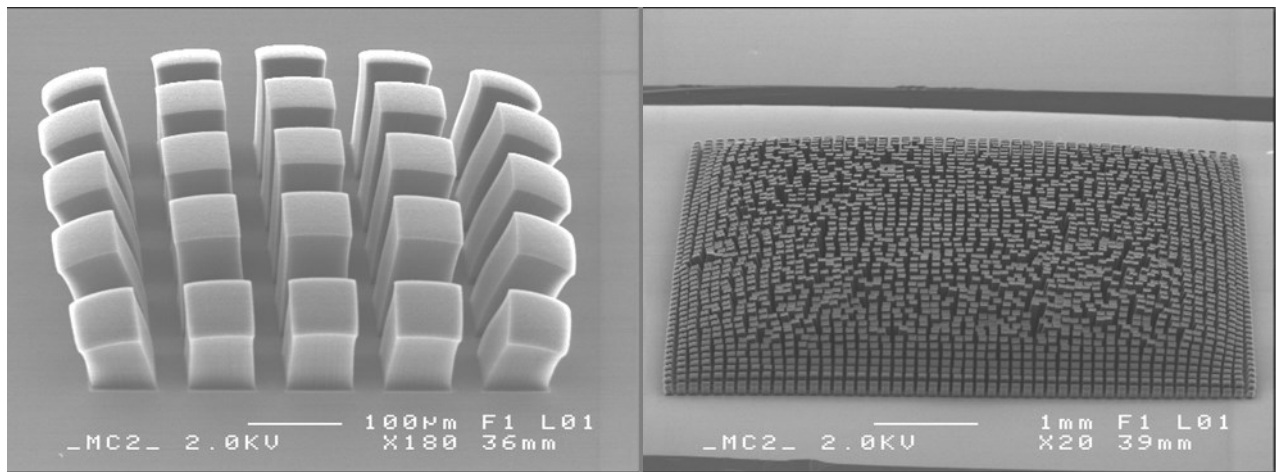


Figure 1. SEM images clearly show the influence of the pattern scale on the length of CNT . (a) Tilt view, (b) top view, and (c) zoomed view of CNT arrays from 50 μm \times 50 μm square made up of pattern with 1 μm feature-size. (d) Line pattern, (e) modified ‘yin-yang’ pattern, (f) zoomed view of CNT arrays from 500 μm x 500 μm square made up of pattern with 10 μm feature-size.

To more systematically study the influence of catalyst area and exclude possible effects from different catalyst feature-sizes on growth^[9], we prepared substrates with different total catalyst area. All substrates were 100

mm² in area and each of them had a catalyst pattern area made up of 70x70 μm² squares with 30 μm spacing between the squares, thus having a catalyst areal density of 55 %. By varying the number of squares, substrates with total catalyst areas of 0.22, 0.94, 3.9, 8.8, 24.7, and 99.4 mm², corresponding to arrays of 5x5, 10x10, 20x20, 30x30, 50x50 and 100x100 squares respectively, but with the identical catalyst areal density within the patterned areas, were prepared. The patterned areas were in the centre of the Si substrates. Six samples with different pattern areas were grown simultaneously for each given furnace temperature (C₂H₂:Ar:H₂=3.0:500:500 sccm, atmospheric pressure, 15 min growth, and 10 nm Al₂O₃ / 1 nm Fe catalyst film). Examples of grown samples are shown in Fig. 2 for a 5x5 and a 50x50 pattern. The gas mixture was chosen to produce the maximum height of CNT grown on unpatterned catalyst films, see Fig. 3. The growth results as a function of patterned catalyst area and furnace temperature are shown in Figs. 4(a) and (b), respectively. The height corresponds to the height of the nanotubes in the centre of the array patterns, determined by scratching the samples and measuring the height from SEM pictures. As can be seen from Fig. 2, the height varies across the pattern with the nanotubes being longer in the central region. Note that the length at the outer edge of the corner squares is very similar in both cases. The highest CNT array was grown at 725°C for all the samples. This agrees well with the optimum furnace temperature for vertical CNT growth determined by Bronikowski for ethylene growth [6] and Duesberg et al. and Geohegan et al. for acetylene growth [9, 10]. When the total patterned area exceeds 9 mm², vertical arrays grow well even at 625 °C, the lowest temperature in this study. The central height of the CNT array increases with increasing patterned area at all studied growth temperatures.



(a)

(b)

Figure 2. SEM images of a 5x5 array (total patterned area 0.22 mm²) and a 50 x 50 array (total patterned area 24.7 mm²).

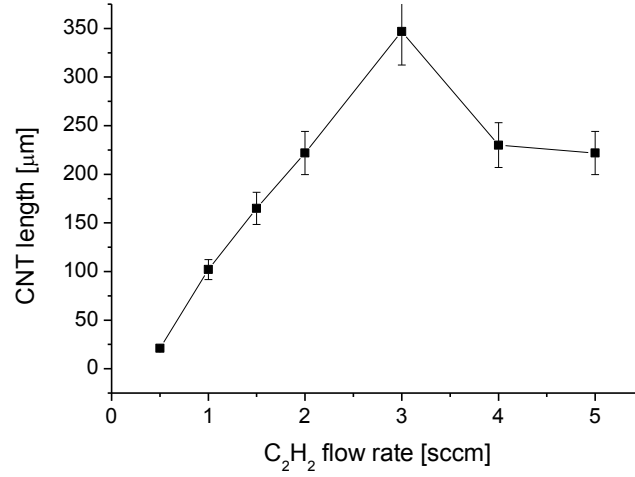


Figure 3. Dependence of CNT length on C₂H₂ flow rate for unpatterned (100 mm²) substrates

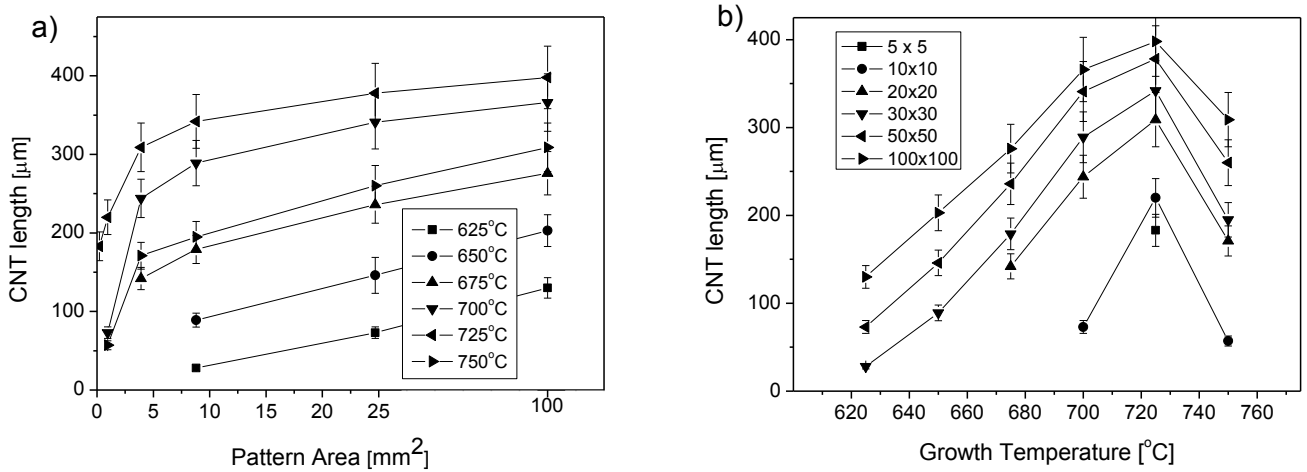


Figure 4. Systematic experimental results for pattern area effect. (a) Plot of CNT length versus total pattern area at different growth temperatures. (b) Plot of CNT length versus growth temperature for different total pattern areas.

If we consider the total amount of carbon deposited per nanotube rather than simply the height at the centre of the arrays the picture looks slightly different. Figure 5 shows TEM images of nanotubes taken from the centre of arrays grown on 0.22 mm² (5x5 array) and 24.7 mm² (50x50 array) patterned areas at a growth temperature of 725 °C, corresponding to the SEM pictures shown in Fig. 2. Clearly, the CNT diameter is smaller and there are fewer walls for the nanotubes grown in the centre of the substrate with the 50 x 50 pattern. The difference in CNT morphology with respect to patterned area is much larger than the difference with growth temperature. We did not detect any significant difference in diameter and number of walls between the same patterned areas

grown at different temperatures (625 °C – 725 °C), in agreement with the observation of Duesberg et al. ^[9]. The lack of significant temperature dependence is in contrast with the results reported by Puretzky et al. ^[11], however their studies covered a larger temperature range (comparing 575 °C growth with 725 °C growth) and their catalyst system was slightly different making a direct comparison problematic. Puretzky et al.'s TEM analysis for nanotubes grown at 725 °C showed predominantly double-walled nanotubes ^[11], in reasonably good agreement with our analysis giving an average number of 3.1 ± 0.9 walls for the centre of the largest patterned area. The results of our analysis are shown in Fig. 6(a) where the average number of walls (squares, left hand axis) and the terminal length in the centre of the nanotube arrays (stars, right hand axis) are plotted as a function of catalyst array area. Although the error bars (corresponding to the standard deviation) are rather large for the TEM analysis, there is a clear trend for a decreasing number of walls and an increasing terminal length as the total patterned area increases. Figure 6(b) shows a plot of the amount of carbon deposited per carbon nanotube as a function of temperature for the different patterned areas. This clearly shows that the change in the diameter and number of walls is the main effect of changing the size of the patterned area, the total amount of carbon deposited in each carbon nanotube (calculated from the average length and average number of walls) is seen to be independent of the patterned area for a given temperature with the possible exception of the smallest patterned area which appears to show a more peaked temperature distribution.

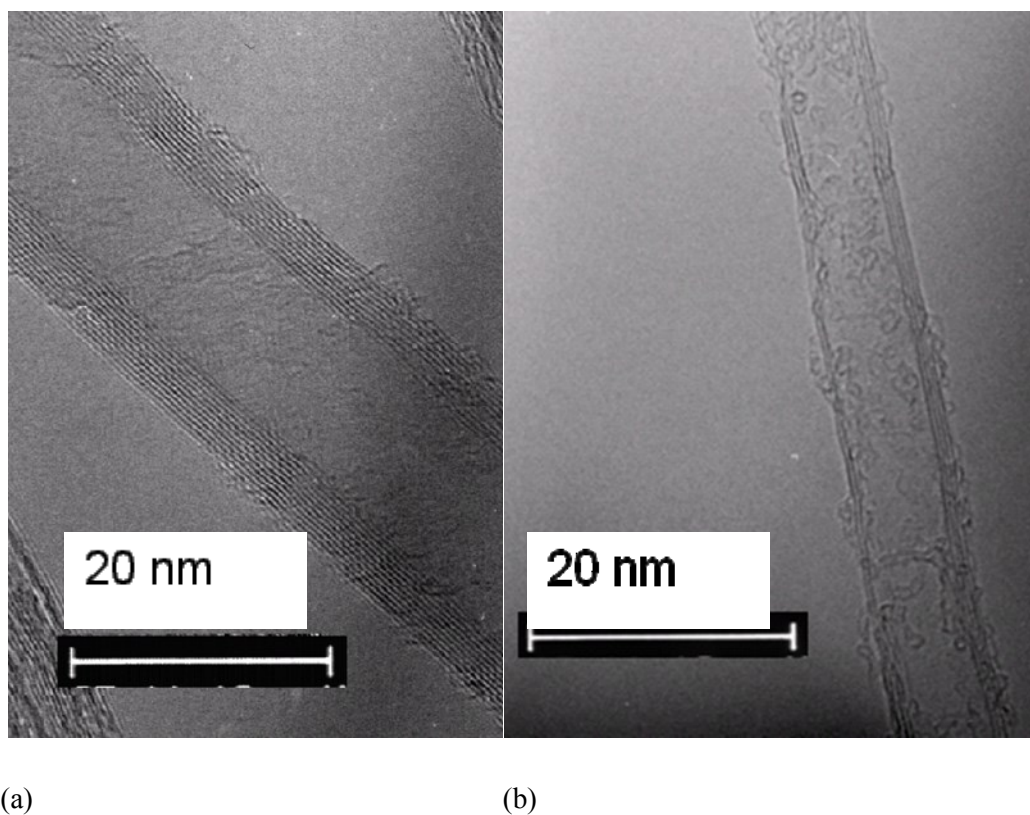


Figure 5. TEM pictures of CNT grown at 725 °C (a) for a 5 x 5 array (patterned area of 0.22 mm²) (b) for a 50 x 50 array (patterned area of 24.7 mm²).

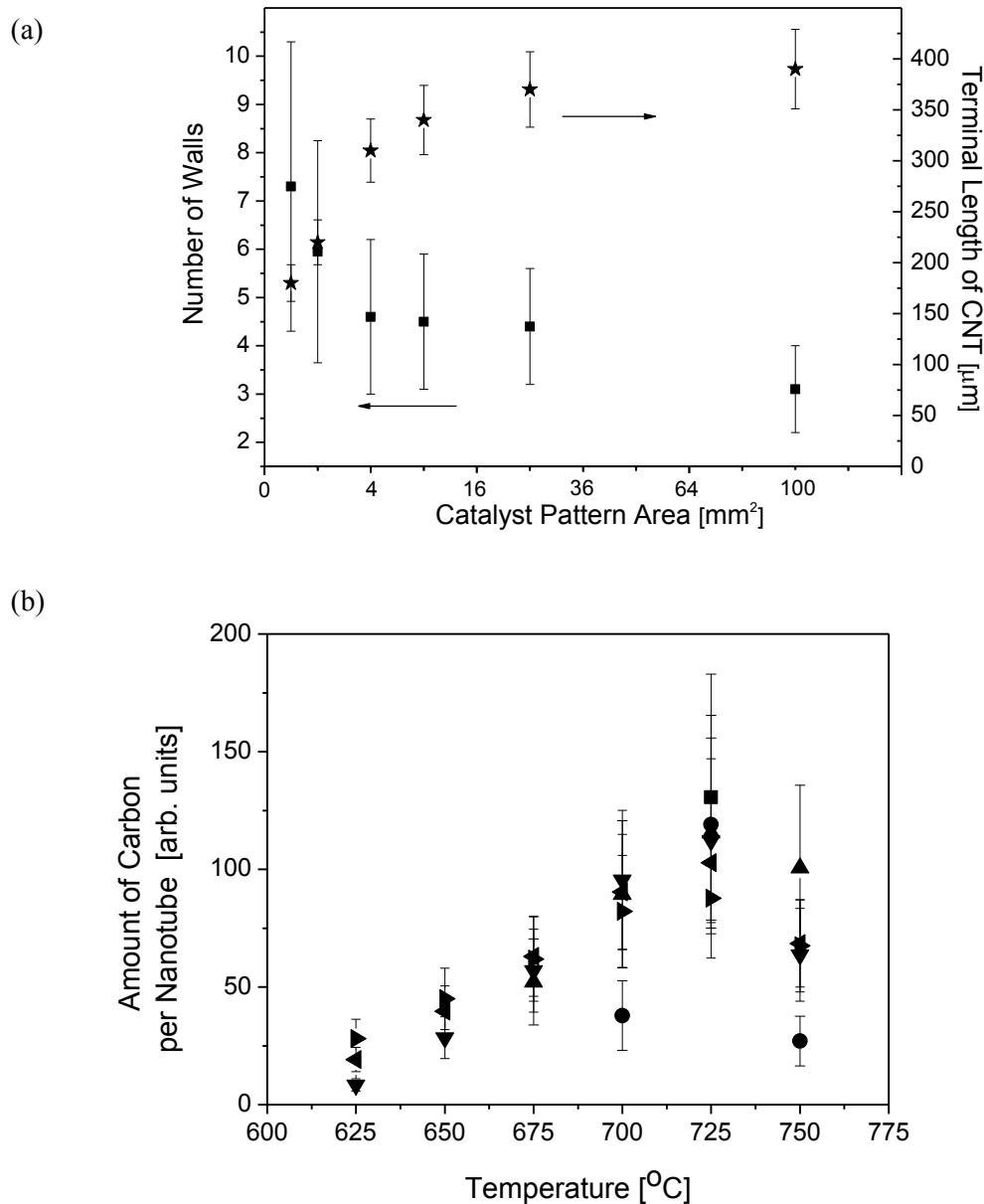


Figure 6. (a) Number of walls (squares) and terminal CNT length (stars) as a function of total pattern area for growth at 725 °C. (b) Amount of carbon deposited in each CNT versus temperature for different array areas; square: 0.22 mm² (5 x 5 array), circles: 0.94 mm² (10 x 10 array), up-triangles: 3.9 mm² (20 x 20 array), down-triangles: 8.8 mm² (30 x 30 array), left-triangles: 24.7 mm² (50 x 50 array), right-triangles: 99.4 mm² (100 x 100 array)

A model has recently been developed to explain the interrelation between single- and multiwall carbon nanotube growth rates for acetylene CVD ^[12]. This showed that the number of walls for a given growth temperature was determined by the interplay of the incident flux of carbon atoms and the carbon diffusion rate through the metal particle. For low temperatures the carbon flux arriving at the particle surface is greater than

the flux through the particle, leading to the formation of multiple walls. For high temperatures, the growth is halted due to poisoning. The model is consistent with the growth rate and TEM results of Poretzky et al. ^[11] and with the “supergrowth” results of Hata et al. where poisoning is repressed ^[13]. Interestingly, the results indicate that the growth rates of all the nanotubes grown are controlled by the SWNT rate. In our case, for a given temperature, growth in the centre of larger patterned areas produce CNTs with less walls but the total amount of carbon deposited per nanotube remains constant. One possible reason for the observations is that the local flux of acetylene (or secondary precursor molecule) at the metal particle surface depends on the total catalyst area. The flux of carbon arriving at the particle is proportional to the local partial pressure of acetylene. For larger patterned areas, the acetylene may be significantly consumed close to the growth region ^[7] thus effectively producing a lower flux of carbon and therefore the growth of nanotubes with fewer walls. Alternatively, gas diffusion through the array may be hindered ^[14] (in our case diffusion from the sides), however this is unlikely to be the reason in our case since the dimensions of the CNT blocks and the relatively large spacings between them are identical, it is only the number of squares that changes.

This is supported by the data in figure 7 showing length of CNTs at different growth times for two different catalyst patterns together with simple approximations of growth at a constant rate for a certain time of growth, τ , until the final length is reached. For the array with 50x50 squares the estimated growth-time of 740 s gives an average growth-rate of 0.6 $\mu\text{m/s}$. For the array with 10x10 squares the estimated τ of 600 s gives an average growth rate of 0.3 $\mu\text{m/s}$. Thus for smaller catalyst patterns growth-rate is slower since more carbon is needed per unit-length when CNTs have more walls.

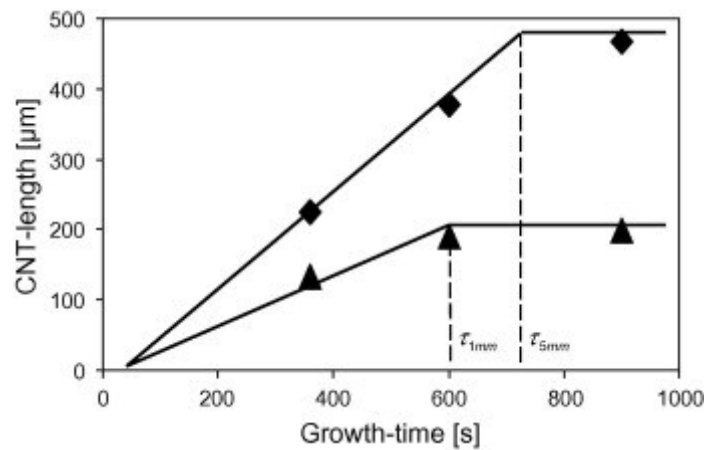


Figure 7. Plot of CNT length versus growth time for two different arrays. Triangles: 0.94 mm² (10 x 10 array); squares: 24.7 mm² (50 x 50 array). Full lines are to guide the eye and dotted lines give an estimate of the time when growth terminates.

The total amount of carbon deposited as nanotubes, for a given temperature, will depend on the competition between growth and poisoning. Since the amount of carbon deposited per nanotube is approximately the same

in our experiments for a given growth temperature, it would appear that the poisoning depends predominantly on the total amount of carbon reaching the particle. For the smaller pattern in figure 7, growth ceases at an earlier time than for larger pattern, which could be expected if poisoning depends on total amount of carbon and smaller patterns experience a higher flux of carbon. This would be consistent with poisoning due to the formation of a carbon coating on the surface of the metal particle.

Another possible explanation for the change in the number of carbon nanotube walls as the catalyst area changes could be related to changes in the catalyst film. Each catalyst area is made up of identical $70 \times 70 \mu\text{m}^2$ catalyst squares, it is only the number of squares that changes for the different catalyst areas under investigation. Thus there is no difference in the catalyst preparation before growth. It is, however, possible that the early growth stages influence the catalyst film. Metal dusting has been shown to play an important role in the growth of multi-walled nanotube films from Fe-catalysed acetylene growth on silicon wafers, without the aluminium oxide buffer layer ^[15]. In order to check any influence of possible catalyst changes in the early stages of growth we have removed the carbon nanotubes after growth by heating in air at 450°C . The surface morphology was then measured by AFM. The results are shown in Figure 8 for a 5×5 array (left) and a 50×50 array (right). No significant difference in surface roughness or island height was found as the number of catalyst squares and therefore the total catalyst area was changed.

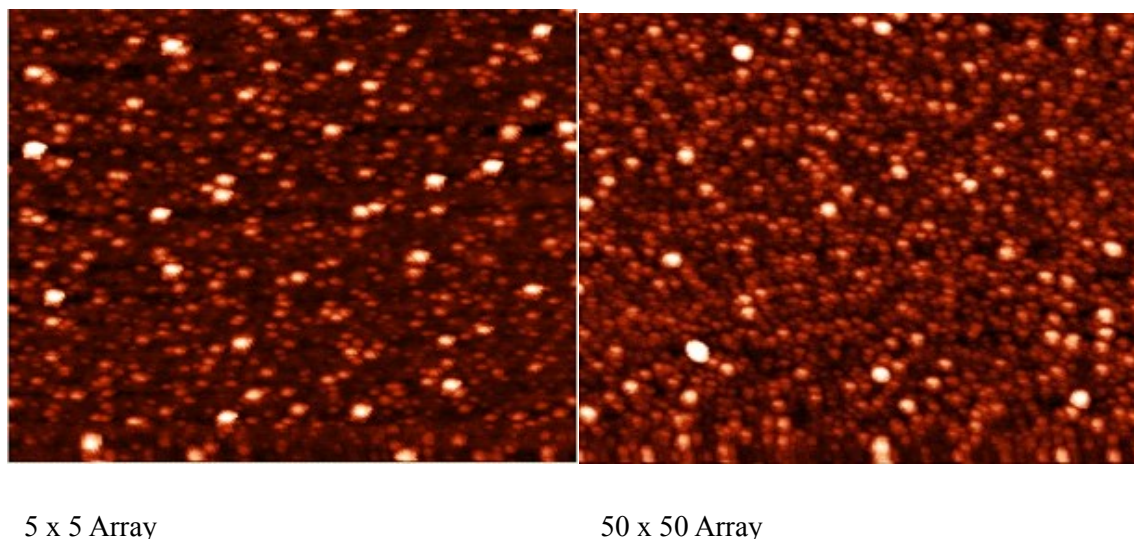


Figure 8. Tapping mode AFM pictures of the catalyst surface after nanotube removal for (left) a 5×5 array and (right) a 50×50 array. Both pictures show the results of a $2 \mu\text{m} \times 2 \mu\text{m}$ scan area. There is no significant difference in the mean surface roughness or particle height from the two samples (Left scan: Average Roughness 2.1 nm, Maximum Height: 28.5 nm, 10 point Average Height: 14.3 nm. Right scan: Average Roughness: 2.2nm, Maximum Height: 29 nm, 10 point Average Height: 14.4 nm).

As seen in Figs. 1(c,f), the alignment of the carbon nanotubes within an individual pillar is significantly

poorer for the pattern with the smaller feature size (1 μm) than for the pattern with the larger feature size (10 μm) at a given temperature. Poorer alignment could be due to a lower nanotube density or to a reduced growth rate (in terms of length per unit time). The density does not appear to be significantly different in the two cases. It is instead possible that the length of nanotubes produced per unit time is the critical parameter for efficient alignment during growth leading to better alignment for the long, few-walled nanotubes. A critical growth rate has been reported for aligned SWNT growth from acetylene^[8] and a critical gas flow rate for aligned MWNT growth from ethylene^[7]. A slower growth rate, as measured in terms of length per unit time, would appear to be the most likely explanation for the poorer alignment observed from the smaller pattern but more studies are needed to clarify this.

3.2. Alignment Dependence on Pattern Size

We now turn our attention to the alignment of the structures formed by CNT arrays. The smaller pattern has a significantly poorer vertical alignment than the larger pattern, as seen in Fig. 1 and discussed above. To investigate this further, CNT were grown on a substrate having catalyst patterned in circular and square patterns with various sizes and densities. For these studies, the growth conditions were identical to those used for the length dependence studies discussed above. The alignment was investigated for different pattern areas, as summarized in Fig. 9. From a large area top-view image, it is clear that larger pillars (left side in Fig. 9(a)) have better vertical alignment than smaller pillars (right side in Fig. 9(a)). Vertically grown CNT pillars with diameters of 50, 20, 10, and 6 μm are shown in Fig. 9(b), 9(c), 9(d) and 9(e), respectively. Here, we evaluated the degree of vertical alignment of the pillars using SEM images by measuring the angle between the substrate plane and the nanotube array axis (Fig. 9(f)). From the results, we conclude that the minimum pattern dimension for growth of isolated freestanding well-aligned CNT pillars under our conditions is approximately 10 μm . Smaller pillars are significantly deflected from the normal and eventually collapse.

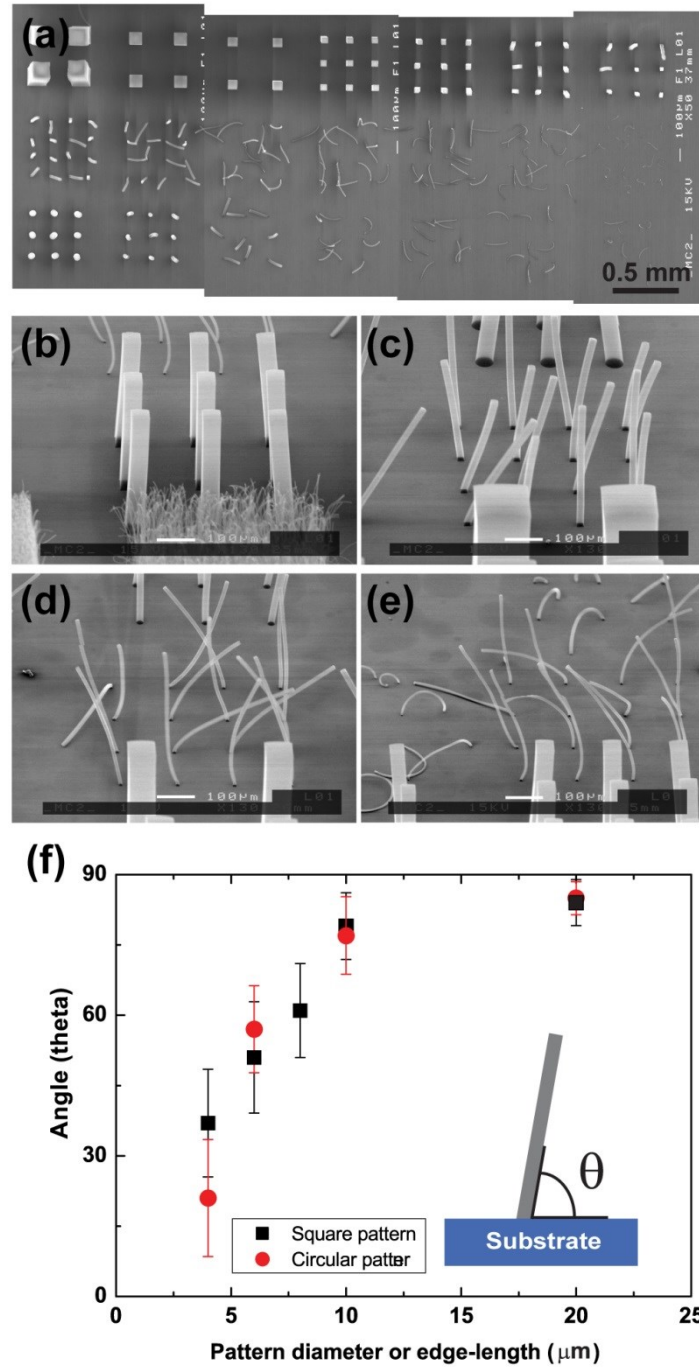
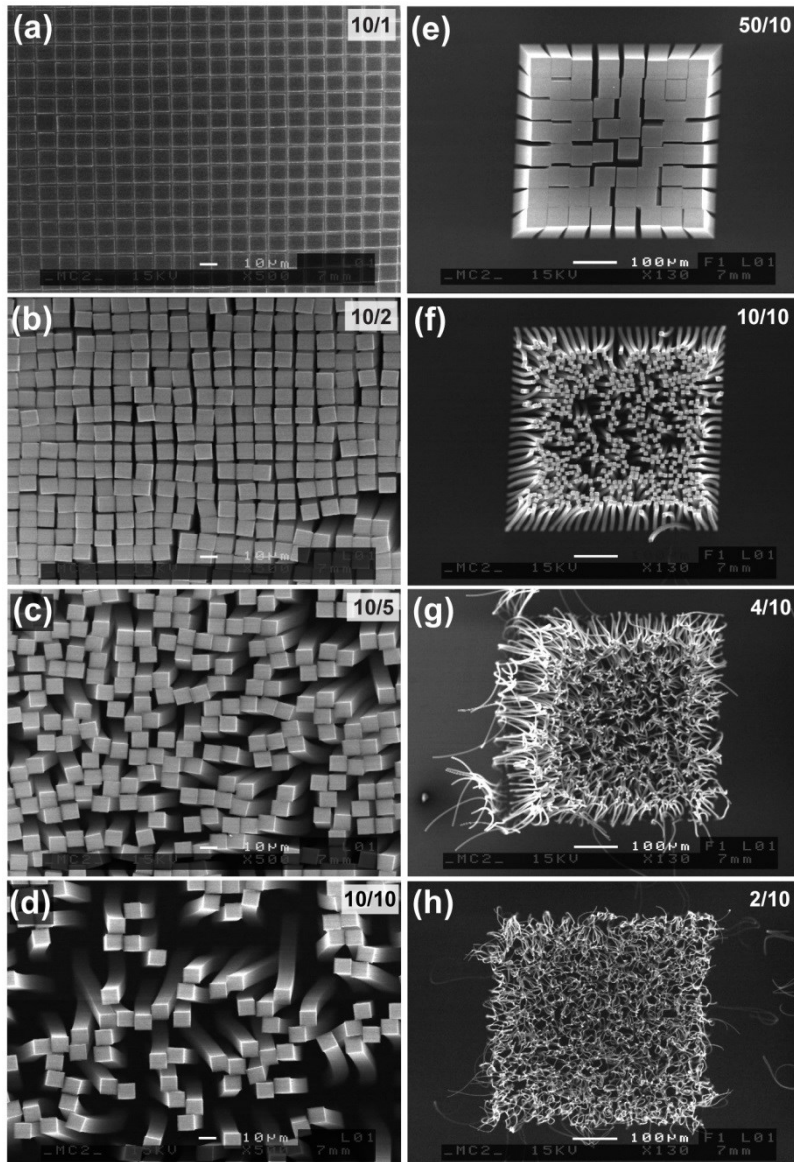


Figure 9. (a) A large area top-view SEM image of vertical CNT arrays with various sizes. (b)-(e) Tilted view of CNT square pillars with different edge lengths. Scale bars are 10 μm. (b) 50 μm, (c) 20 μm, (d) 10 μm, and (e) 8 μm. (f) Pattern size dependence of vertical alignment.

However, the situation is changed when CNT pillars have close neighbours. A significantly enhanced vertical alignment of the CNT pillars can be achieved by changing not only the pattern size but also the edge-to-edge distance between the individual pillars even for pillars below the critical individual alignment dimension of 10 μm.

Typical growth results are shown in Figs. 10 and 11. The left hand column of Fig. 10 shows the influence of the pillar spacing for an individual pillar dimension of $10 \times 10 \mu\text{m}$. The more densely packed CNT pillars clearly have better vertical alignment. Note that for these studies the CNT are growing to the same height, independent of the pillar spacing (supporting our argument above that gas diffusion is not the limiting factor). The right hand column shows the influence of the individual pillar dimension for a fixed spacing of $10 \mu\text{m}$. For the large pillar dimensions (Fig. 10(e) and 10(f)), the individual CNT pillars are free-standing and preserve their collective structure. For the smaller patterns, Fig. 10(g) and 10(h), some neighbouring CNT pillars touch each other and a few pillars located at the edge of the pattern are deflected outwards (Fig. 10(g) and 10(h)). Very similar behaviour is seen in Fig. 11 for $2 \mu\text{m}$ (left side) and $4 \mu\text{m}$ (right side) pillars with different spacings. There appears to be an interaction between the pillars that induces vertical alignment, similar to the crowding effect at the individual CNT level, leading to vertically aligned nanotubes. Thus, the value of the pillar dimension/pillar spacing ratio is also an important factor for determining vertical alignment of the pillars.



← **Figure 10.** SEM images showing dependence of vertical alignment of CNT arrays on pattern dimension. (a)-(d) The same pattern size ($10 \mu\text{m}$) with different spacing (1 , 2 , 5 and $10 \mu\text{m}$). (e)-(h) The same spacing ($10 \mu\text{m}$) with different pattern size (50 , 10 , 4 and $2 \mu\text{m}$).

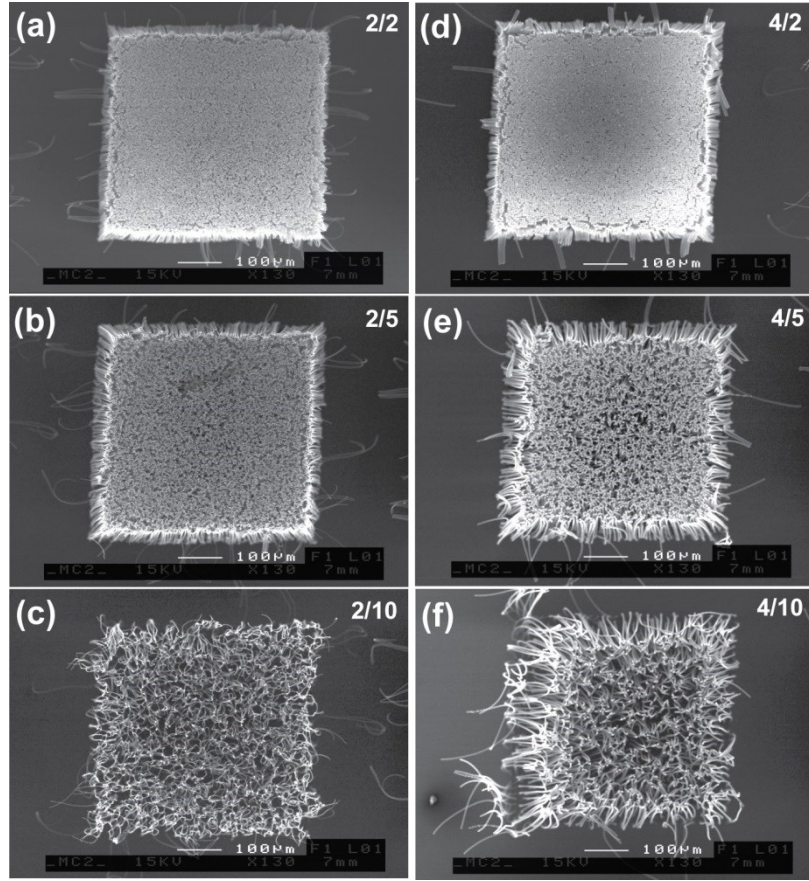


Figure 11. SEM images showing dependence of vertical alignment of CNT arrays on pattern dimension. (a)-(c) The same pattern size (2 μm) with different spacing (2, 5 and 10 μm). (d)-(f) The same pattern size (4 μm) with different spacing (2, 5 and 10 μm).

The porosity of vertically aligned arrays of MWNT has been reported to be 92 % for TCVD growth by Geohegan et al. ^[10] and 87 % for PECVD growth by Jönsson et al. ^[16]. Although the overall view of such vertically aligned CNT arrays appears to show very good alignment, on the individual nanotube scale it can be seen that the alignment is far from perfect. The more dense PECVD structures do, however, typically have better local alignment than the TCVD ^[17]. The determined porosities for films of vertically aligned MWNT correspond to an individual CNT diameter/spacing ratio of 0.5 and 0.7 for the thermal and plasma CVD arrays, respectively. If we can extend the results of our CNT pillar studies to the individual CNT level, one could consider that significantly better alignment on the individual CNT level might be achieved if the porosity of the CNT films could be decreased to 80% or less, corresponding to diameter/spacing ratios of 1 or higher. Such CNT films with improved local CNT alignment could be beneficial e.g. for applications as interconnects within microelectronics.

4. Summary

In summary, we demonstrate the effect of catalyst pattern geometry on the growth behavior of CNT arrays. Larger catalytic patterns produce longer CNT arrays, however, the amount of carbon deposited per nanotube is independent of pattern size. This is related to the local partial pressure of acetylene. For large patterns, acetylene becomes depleted leading to a lower local partial pressure and lower carbon flux at the metal particle. In agreement with a recent model by Wood et al. ^[12], this leads to the growth of carbon nanotubes with a lower number of walls than for the smaller catalyst areas where depletion is less noticeable. Growth stops due to a process that depends only on the total amount of carbon reaching the metal particle, consistent with the formation of a carbon coating. In addition, the vertical alignment of CNT pillar arrays is seen to significantly depend on the pattern geometry. Even when pillars are too small to produce individual vertically aligned structures ($< 10\ \mu\text{m}$), they will form well-aligned arrays if the pillar spacing is on the order of the individual pillar dimension.

References

- [1] Fan, S., Chapline, M.G., Franklin, N.R., Tomblor, T.W., Cassell, A.M., Dai, H. "Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties" *Science* 1999; 283: 512-514.
- [2] Xu, T., Wang, Z., Miao, J., Chen, X., Tan, C.M., "Aligned carbon nanotubes for through-wafer interconnects" *Appl. Phys. Lett.* 2007; 91: 042108.
- [3] Jung, Y.J., Kar, S., Talapatra, S., Soldano, C., Viswanathan, G., Li, X., et al., "Aligned Carbon Nanotube-Polymer Hybrid Architectures for Diverse Flexible Electronic Applications", *Nano Lett.* 2006; 6: 413-418.
- [4] Kreupl, F., Graham, A.P., Duesberg, G.S., Steinhögl, W., Liebau, M., Unger, E., et al., "Carbon nanotubes in interconnect applications", *Microelectronic Eng.* 2002; 64: 399-408.
- [5] Jang, J.E., Cha, S.N., Choi, Y., Amaratunga, G., Kang, D.J., Hasko, D.G., et al. "Nanoelectromechanical switches with vertically aligned carbon nanotubes", *Appl. Phys. Lett.* 2005; 87: 163114.
- [6] Bronikowski, M.J., "CVD growth of carbon nanotube bundle arrays", *Carbon* 2006; 44: 2822-2832.
- [7] Hart, A.J., Slocum, A.H., "Rapid Growth and Flow-Mediated Nucleation of Millimeter-Scale Aligned Carbon Nanotube Structures from a Thin-Film Catalyst", *J. Phys. Chem. B* 2006; 110: 8250-8257.
- [8] Eres, G., Kinkhabwala, A.A., Cui, H., Geohegan, D.B., Puretzky, A.A., Lowndes, D.H., "Molecular Beam-Controlled Nucleation and Growth of Vertically Aligned Single-Wall Carbon Nanotube Arrays", *J. Phys. Chem. B* 2005; 109: 16684-16694.
- [9] Duesberg, G., Graham, A.P., Kreupl, F., Liebau, M., Seidel, R., Unger, E., Hoenlein, W., "Ways towards the scaleable integration of carbon nanotubes into silicon based technology", *Diamond and Related Materials* 2004;13: 354-361.
- [10] Geohegan, D.B., Puretzky, A.A., Ivanov, I.N., Jesse, S., Eres, G., Howe, J.Y., "*In situ* growth rate measurements and length control during chemical vapor deposition of vertically aligned multiwall carbon nanotubes", *Appl. Phys. Lett.* 2003; 83: 1851-1853.
- [11] Puretzky, A.A., Geohegan, D.B., Jesse, S., Ivanov, I.N., Eres, G., "In situ measurements and modelling of carbon nanotube array growth kinetics during chemical vapor deposition", *Appl. Phys. A* 2005; 81: 223-240.
- [12] Wood, R.F., Pannala, S., Wells, J.C., Puretzky, A.A., Geohegan, D.B., "Simple model of the interrelation between single- and multiwall carbon nanotube growth rates for the CVD process", *Phys. Rev. B* 2007; 75: 235446.
- [13] Hata, K., Futaba, D.N., Mizuno, K., Namai, T., Yumara, M., Iijima, S., "Water-Assisted Highly Efficient

Synthesis of Impurity-Free Single-Walled Carbon Nanotubes”, *Science* 2004; 306: 1362-1364.

- [14] Hart, A.J., van Laake, L., Slocum, A.H., “Desktop Growth of Carbon-Nanotube Monoliths with In Situ Optical Imaging”, *Small* 2007; 3: 772-775.
- [15] Yao, Y., Falk, L.K.L., Morjan, R.E., Nerushev, O.A., Campbell, E.E.B., “Nucleation and aligned growth of multi-wall carbon nanotube films during thermal CVD”, *Carbon* 2007; 45: 2065-2071.
- [16] Jönsson, M., Nerushev, O.A., Campbell, E.E.B., “In situ growth rate measurements during plasma-enhanced chemical vapour deposition of vertically aligned multiwall carbon nanotube films”, *Nanotechnology* 2007; 18: 305702.
- [17] Morjan, R.E., Maltsev, V., Nerushev, O., Yao, Y., Falk, L.K.L., Campbell, E.E.B., “High growth rates and wall decoration of carbon nanotubes grown by plasma-enhanced chemical vapour deposition”, *Chem. Phys. Lett.* 2004; 383: 385-390.